

学位論文の要約

題目 Polymorphs and Functional Properties of Crystalline Membranes of Fluorite Oxides
(蛍石型酸化物の結晶メンブレン膜における結晶多型と機能特性)

氏名 SHEN YUFAN

Ferroelectric hafnia with fluorite structures attracted tons of attention due to its compatibility with the modern semiconductor industry and robust ferroelectricity down to nanometer size. However, challenges remain in further exploring the intrinsic stability of the ferroelectric phase and understanding its unique stabilization mechanisms due to the polycrystalline nature of hafnia thin films, which makes it difficult to probe their atomic structure for deeper understanding.

In this thesis, the candidate aims to understand the stabilization mechanism of metastable structures in hafnia, and to achieve freestanding membranes of hafnia and other binary oxides with fluorite structure for further exploring their intrinsic properties and phase structures without external support. The detailed crystal structures and electrical properties are discussed in this thesis.

[1] Stabilization of Ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ Epitaxial Thin Film via Interfacial Reconstruction

Discoveries of metastable ferroelectric HZO epitaxially grown on structurally dissimilar perovskite oxides have triggered intensive investigations on the ferroelectricity in materials that are nonpolar in bulk form. Nonetheless, the growth mechanism for the unique fluorite-perovskite heterostructures has yet to be fully explored. Here, we show that the metastable ferroelectric HZO films can be stabilized even on a 1-unit-cell-thick perovskite $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ buffer layer. In collaboration with scanning transmittance electron microscopy (STEM)-based characterizations, we show that monolayer reconstructions driven by the valence-dependent interfacial redox reaction of Mn, along with intralayer electron transfers, play a vital role in the formation of a unique heterointerface between the two structurally dissimilar oxides, providing the template monolayer that facilitates the epitaxial growth of the metastable HZO films.

Our findings offer significant insights into the stabilization mechanism of the ferroelectric HZO, and this mechanism could be extended for exploring functional metastable phases of various metal oxides

[2] Ferroelectric freestanding hafnia membranes with metastable rhombohedral structure down to 1-nm-thick

We fabricated stable 1-nm-thick hafnia membranes exhibiting the metastable rhombohedral structure and out-of-plane ferroelectric polarizations as large as $13 \mu\text{C}/\text{cm}^2$. We also found that the rhombohedral phase transforms into another metastable orthorhombic phase without the ferroelectricity deteriorating as the thickness increases. Our results reveal the key role of the rhombohedral phase in the scale-free ferroelectricity in hafnia and also provide critical insights into the formation mechanism and phase stability of the metastable hafnia. Moreover, ultrathin hafnia membranes enable heterointerfaces and devices to be fabricated from structurally dissimilar materials beyond structural constrictions in conventional film-growth techniques.

[3] Ultrathin Freestanding Membranes of ZrO_2 with Metastable Structures and Strain-dependent Electrical Properties

In this study, we fabricated freestanding ZrO_2 (ZO) membranes with metastable crystal structures by exfoliating ZO epitaxial layers from $\text{ZrO}_2/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3$ heterostructures. By combining the results of first-principles calculations, we found that with increasing thickness up to 15 nm, ZO membranes undergo structural relaxation from the metastable tetragonal structure to a metastable orthorhombic one. In addition, the dielectric constant of the tetragonal ZO is susceptible to the strain accumulated in the ZO layer. The strain release associated with the exfoliation of ZO layers leads to an increase in the dielectric constant (to ~ 25). ZO membranes with high dielectric constants could be utilized in energy storage capacitors.